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Experimental study on CO and CO₂ emissions from spontaneous heating of coals at varying temperatures and O₂ concentrations

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Abstract

Laboratory experiments were conducted to investigate carbon monoxide (CO) and carbon dioxide (CO₂) emissions from spontaneous heating of three U.S. coal samples in an isothermal oven at temperatures between 50 and 110 °C. The oxygen (O₂) concentration of an oxygen/nitrogen (N₂) mixture flowing through the coal sample was 3, 5, 10, 15, and 21%, respectively. The temperature at the center of the coal sample was continuously monitored, while the CO, CO₂, and O₂ concentrations of the exit gas were continuously measured. The results indicate that the CO and CO₂ concentrations and the CO/CO₂ ratio increased when the initial temperature was increased. As the inlet O₂ concentration increased, the CO and CO₂ concentrations increased, while the CO/CO₂ ratios tended to converge to the same value. The ratio of CO/CO₂ was found to be independent of coal properties, approaching a constant value of 0.2. The maximum CO production rate correlated well with the maximum coal temperature rise. The apparent order of reaction for coal oxidation was estimated to be between 0.52 and 0.72. The experimental results in this study could be used for early detection and evaluation of a spontaneous heating in underground coal mines.

Keywords

Spontaneous heating; Coals; CO and CO₂ emissions; Detection

1. Introduction

Spontaneous combustion has long been a problem in the mining, storage, and transport of coal because coal can react with O₂ in the air at ambient temperature, producing heat. For the period 1990–2006, a total of 25 reported underground coal mine fires in the U.S. were caused by spontaneous combustion. The risk of an explosion ignited by a spontaneous combustion fire is also present in those mines with appreciable levels of accumulated methane. Spontaneous combustion usually starts as a low temperature coal oxidation reaction. This chemical reaction between coal and O₂ at low temperatures is complex and still not well understood. Many laboratory-scale experiments have been conducted to

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understand the effects of various parameters on the spontaneous heating process, such as particle size, moisture in the air, moisture content of coal, O₂ concentration, initial temperature, mineral matter, and coal aging. In practice, the heat and gaseous products from a spontaneous heating are the two most important parameters for detecting and preventing a spontaneous heating event. If the heat is not dissipated fast enough, it causes the coal temperature to rise, and this temperature rise can accelerate the coal oxidation process. CO and CO₂ are the two major gaseous products produced from the spontaneous heating. Their presence and their concentrations in the gas stream can be used for early detection and to determine the state of a spontaneous heating. In order to more effectively detect and correctly assess the state of a spontaneous heating, the characteristic properties of CO and CO₂ emissions from coal during a spontaneous heating event need to be investigated.

A few studies on the CO and CO₂ emissions in spontaneous heating have been reported in the literature. Chamberlain and Hall (1973) found that CO is the most sensitive indicator of the early stages of coal oxidation, and the continuous monitoring of this gas provides the earliest detection of self-heating. Itay, Hill, and Glasser (1989) studied the low temperature oxidation of coal for a temperature range of 25–140 °C. The temperature-time history of a sample was followed, and the gaseous products (CO and CO₂) were analyzed. The authors suggested that the first step in the oxidation is a reversible physical absorption, and that CO and CO₂ are produced via a secondary reaction. Adamus, Sancer, Guranova, and Zubicek (2011) investigated the accuracy of interpretation of mine gases in connection with the use of laboratory-verified gas characteristics of thermal oxidation of coal. Kaji, Hishinuma, and Nakamura (1985) studied the low-temperature oxidation of five coals in the temperature range from 30 to 250 °C. The rates of formation of CO and CO₂ were correlated to the internal surface area and the oxygen contents of the coals. Wang, Dlugogorski, and Kennedy (2002) studied the formation of CO₂, CO and H₂O during the low-temperature oxidation of a bituminous coal using an isothermal flow reactor. The rates of consumption of O₂ and the formation of carbon oxides were measured for different O₂ concentrations in the gas stream and at varied initial temperatures. Cliff, Clarkson, Davis, and Bennett (2000) conducted large-scale tests for detection and monitoring of spontaneous combustion of coal. They found that the best indicators of spontaneous combustion are those that are independent of airflow, such as the amount of CO released and Graham's ratio, but that even these indicators have some limitations. Chakravorty and Woolf (1979) found that the absolute level of CO in the mine air, whether high or low, is not of great significance but that an increasing trend is indicative of heating. In our previous experimental study, the CO/CO₂ ratio was found to be independent of the ventilation rates (Yuan & Smith, 2011).

This paper attempts to provide experimental data to improve the early detection of spontaneous heating in underground coal mines. In this study, laboratory-scale experiments were conducted to investigate the effect of initial temperature, O₂ concentration, and coal properties on the CO and CO₂ emissions during the spontaneous heating of three U.S. coals. The relationship between CO production rate and the coal temperature rise was also examined.

2. Experimental

Experiments were conducted in an isothermal oven. The oven temperature can be set from 40 to 200 °C, within an accuracy of ± 0.5 °C. Hereafter, the oven temperature is referred to as the initial temperature. Fig. 1 shows a schematic of the experimental setup. During the test, the coal sample is contained in a brass wire mesh basket, 6-cm-diameter by 10-cm-high, which is enclosed in a brass container, and placed in the center of the oven. Based on the available volume of the isothermal oven, the height of 10 cm was chosen as the appropriate height of coal sample in this study. A different height may lead to a slightly different result. The container has ports in the bottom and top to allow gas to flow through the coal sample. Initially, the coal sample is heated to a selected temperature while exposed to a flow of N₂ at a flow rate of 200 cm³/min. The gas is pre-heated to the oven temperature by passing through heat exchange coils in the oven. The inlet gas is then switched to the O₂/N₂ mixture with a predetermined O₂ concentration at the same flow rate of 200 cm³/min. Commercially available O₂/N₂ mixtures with O₂ concentration of 3, 5, 10, 15, and 21% are used in the study.

With the O₂/N₂ mixture flowing through the coal sample, coal oxidation takes place. Three 0.5-mm-diameter type-K thermocouples are placed at the center of the coal, 3 cm above and below the coal center, respectively, to monitor the coal temperature. The exhaust gas exits the container and travels through a water trap before passing through O₂, CO, and CO₂ gas analyzers. The CO and CO₂ concentrations are measured continuously using infrared gas analyzers, while the O₂ concentration is measured continuously by a paramagnetic O₂ analyzer. The instrument measurement ranges are 0–5000 ppm for CO, 0–10,000 ppm for CO₂, and 0–25% for O₂. Before a test starts, the O₂, CO, and CO₂ gas analyzers are calibrated using standard calibration gases. Tests are terminated when the coal temperature is either decreasing or the coal temperature reaches 250 °C.

The three coal samples used in the study are bituminous coals from the western United States. The proximate and ultimate analyses for the coal samples are given in Table 1. Table 2 shows activation energies, minimum self-heating temperatures (SHT) and relative self-heating tendencies for the three coals. The activation energy of coal is measured using the heat release method as described in a previous publication (Yuan & Smith, 2012). The SHT is a measure of a coal's reactivity, and is calculated based on the method established by Smith and Lazzara (1987) using coal analysis data. The relative self-heating tendency of coal is determined based on its SHT value. To prepare the coal for testing, lumps of fresh coal are passed through a jaw crusher and then sieved. A 150-gram sample of the 100 × 200 mesh (75 × 150 μm) size fraction is then dried in the oven under N₂ at 67 °C with a flow rate of 200 cm³/min prior to the experiment.

3. Experimental results and discussion

3.1. Effect of initial coal temperature on CO and CO₂ emissions

Experiments were conducted on coal sample A at initial temperatures ranging from 50 to 100 °C. Fig. 2 shows the CO concentration of the exit gas at these different initial temperatures for an O₂ concentration of 21%. At initial temperatures of 80 °C and below,

the CO concentration increased at the start of the test and then slowly decreased. The magnitude of the CO initial concentration rise increased with increased initial temperature. At an initial temperature of 90 °C, the CO concentration rapidly increased, reaching a maximum value of 1300 ppm. At an initial temperature of 100 °C, a thermal runaway occurred and the CO concentration increased very rapidly. This same pattern was also observed for the CO₂ concentration, with the CO₂ concentrations being much higher than the CO concentration. Fig. 3 shows the corresponding center coal temperature increases at the different initial temperatures for coal sample A. At initial temperatures of 80 °C and below, the maximum temperature increase ranged from 3 to 7 °C, indicating a low oxidation rate, thus producing less CO and CO₂.

Fig. 4 shows the CO/CO₂ ratio for coal sample A for the previously described experiments. During the tests, CO was always generated earlier than CO₂. The CO₂ concentration increased beyond the CO value very quickly after CO₂ was detected. The CO/CO₂ ratio was initially high when the CO₂ value was lower than the CO value, and then decreased quickly to the value of 1 when the CO₂ value intercepted the CO value. Therefore, the CO/CO₂ ratio was plotted starting from the value of 1. The ratios at different initial temperatures seem to converge to the value of 0.2. This is in agreement with results from tests where ventilation rates were varied for the same coal sample (Yuan & Smith, 2011). After closer examination of the data in Fig. 4, it can be seen that the CO/CO₂ ratio did increase slightly with the initial temperature, except at 70 and 80 °C. Similar experiments were conducted for the other coal samples, B and C. The CO/CO₂ ratios, shown in Fig. 5, for coal sample C at different initial temperatures, show more clearly that the CO/CO₂ ratio increased with the increase of initial temperature. This finding is consistent with the results in Fig. 5 that the CO/CO₂ ratio decreased slower at higher temperatures than at lower temperatures. Itay et al. (1989) also found that the value of CO/CO₂ ratio at the end of a run in their tests changed from 0.19 to 0.5 as the temperature changed from 56 to 140 °C. The experimental results in the current study indicate that the CO/CO₂ ratio does increase with an increasing initial temperature, but that the ratio value and magnitude of increase with increasing temperature will be dependent on the type of coal.

3.2. Effect of O₂ concentration on CO and CO₂ emissions

In order to investigate the effect of O₂ concentration on CO and CO₂ emissions from spontaneous heating, experiments were conducted for coal sample A with different inlet O₂ concentrations at initial temperatures of 90, 100, and 110 °C, respectively. Fig. 6 shows the CO concentrations for the different O₂ concentrations at an initial temperature of 90 °C. As the O₂ concentration increased from 3% to 15%, the CO concentration increased slowly, while as the O₂ concentration increased from 15% to 21%, the CO concentration increased significantly. The same pattern of increase was also observed for the CO₂ concentration. Fig. 7 shows the corresponding coal center temperatures for the different O₂ concentrations for coal sample A. With the inlet O₂ concentration below 21%, the coal center temperature rise was less than 10 °C. With the O₂ concentration of 21%, the center coal temperature increased about 48 °C. It is worth noting that for O₂ concentrations ranging from 3% to 15%, there is still oxidation taking place. The rate of reaction is reduced in proportion to the O₂ concentration. This suggests that any amount of inertization helps to reduce the oxidation

rate and that it may not be necessary to inertize an environment to a very low O₂ concentration to prevent spontaneous heating. Similar results were reported by Schmidt, Lohrer, and Krause (2003). They found that an exothermic effect due to oxidation occurred even at O₂ volume fractions as low as 1.3% for some coal dusts. For volume fractions of O₂ between 21% and 12%, only a minor increase of both the self-ignition temperatures and the induction periods was observed. A more pronounced increase of the self-ignition temperature and the induction period occurred for the volume fraction of O₂ below 12%.

Comparing Figs. 2 and 6, the inlet O₂ concentration has a similar effect on the CO emission as the initial temperature. After further analysis, it can be found that the CO concentration seemed to correlate with the center coal temperature rise. Fig. 8 shows the maximum CO production rates versus the maximum center coal temperature rise for coal sample A for all experimental data at different initial temperatures with the inlet O₂ concentration of 21%, and experimental data with different inlet O₂ concentrations at initial temperatures of 90, 100, and 110 °C, respectively. The results indicate that the maximum CO production rate increased proportionally with the increase of maximum center coal temperature rise.

3.3. Apparent reaction order of coal oxidation

The reaction rate of the coal oxidation can be estimated using the rate of O₂ consumption as measured in the exit gas. In this study, it was found that, if there was no thermal runaway, the O₂ concentration reached the minimum value about 15 min after the gas was switched from pure N₂ to the O₂/N₂ mixture. This minimum O₂ concentration value was used to calculate the rate of O₂ consumption. The effect of O₂ concentration in the inlet on the O₂ consumption rate by coal can be represented by a power-law relationship:

$$R_{O_2} \propto C_{O_2}^n$$

where R_{O_2} is the rate of O₂ consumption, C_{O_2} is the inlet O₂ concentration, and n is the apparent reaction order of O₂ consumption. Fig. 9 shows the rate of O₂ consumption versus the inlet O₂ concentration plotted on a double-logarithm graph. The apparent reaction order was estimated by linear least-squares fitting to the experimental data. The apparent reaction order was 0.52, 0.63, and 0.72 at initial temperatures of 90, 100, and 110 °C, respectively, indicating that the apparent reaction order increased with the increase of the initial temperature. These results are consistent with other reported results. Schmidt and Elder (1940) reported that the value of the apparent order of the reaction in low-temperature oxidation studies of some U.S. coals is about 0.61. Kaji et al. (1985) found that the orders of reaction for CO₂ and CO formation were 0.50 and 0.54, respectively, with respect to O₂ for an Australia coal at 150 °C.

3.4. Effect of O₂ concentration on the CO/CO₂ ratio

Figs. 10 and 11 show the CO/CO₂ ratios for coal sample C with different inlet O₂ concentrations at initial temperatures of 90, 100 °C, respectively. With the O₂ concentration of 3% at the initial temperature of 90 °C, the CO₂ concentration measurements did not have enough precision and were not included here. At the initial temperature of 90 °C, the CO/CO₂ ratios decreased to between the values of 0.1 and 0.3. At the initial temperature of

100 °C, the CO/CO₂ ratios also decreased and eventually converged around the value of 0.2. The results indicate that as the initial temperature increased, the CO/CO₂ ratios with different O₂ concentrations converged to the same value of 0.2. These results are qualitatively consistent with the findings of Wang et al. (2002). They found that the amount of generated CO₂ is proportional to that of CO, and is independent of the sample particle size and O₂ concentration in the gas stream. The molar ratio of CO₂/CO production is found empirically to be about 3, leading to a CO/CO₂ ratio of 0.33.

3.5. Effect of coal properties on the CO/CO₂ ratio

It is interesting to note that the CO/CO₂ ratios in Figs. 4 and 11 both approach the value of 0.2 for two different coal samples under different experimental conditions. To examine the effect of coal properties on the CO/CO₂ ratio, Fig. 12 shows the CO/CO₂ ratios for three coals at the initial temperature of 90 °C with the inlet O₂ concentration of 15%. The CO/CO₂ ratios decreased and were eventually between the values of 0.4 and 0.2. The coal sample C has the largest value of CO/CO₂ ratio, while the coal sample A has the least one. When the initial inlet O₂ concentration was at 21%, the CO/CO₂ ratios for three coals were eventually around the value of 0.2, as shown in Fig.13. The results indicate that the value of CO/CO₂ ratio for different coals tends to converge to the value of 0.2 as the inlet O₂ concentration is at 21%.

3.6. Correlation between coal temperature and CO concentration for three coals

Figs. 14 and 15 show the center coal temperature rise and CO concentrations, respectively, for three coals at the initial temperature of 90 °C and the inlet O₂ concentration of 21%. Clearly, coal sample A had the largest temperature and CO concentration rise, while coal sample C had the smallest increases. These results correlate well with the activation energies and SHTs of three coals shown in Table 2. The results indicate that the most reactive coal sample, A, had the largest center temperature and CO concentration rise.

The maximum CO production rate and the maximum center coal temperature for the three coals are shown in Fig. 16. The relationship can be represented well by the equation:

$$\text{CO production rate} = 3.2 \times 10^{-11} * \Delta T - 5.4 \times 10^{-11}$$

The production rate is in kmol/(kg coal*s), and the temperature rise, T , is in °C. This equation may be used to estimate the temperature of coal in a spontaneous heating event from measured CO concentration and ventilation flow rate.

4. Conclusions

Laboratory-scale experiments were conducted to investigate the effects of initial temperature and the inlet O₂ concentration on the CO and CO₂ emissions for three bituminous coals of different reactivities. The CO and CO₂ emissions increased as the initial temperature increased. The CO/CO₂ ratio was also found to increase with the increase of the initial temperature. This increase became less significant for the more reactive coal. As with the initial temperature, the inlet O₂ concentration had a similar effect on spontaneous heating. In

experiments using inlet O₂ concentrations ranging from 3% to 15%, there were no significant changes in CO and CO₂ emissions for O₂ concentration at or below 15%, suggesting that spontaneous heating of coal may be prevented before a space is inertized to a very low O₂ concentration.

It was also found that the maximum CO production rate correlated well with the maximum center coal temperature rise for three U.S. coals independently of initial temperature and O₂ concentration. This relationship may be used to estimate coal temperature from measured CO concentration, and thus may be a potential method for detecting spontaneous combustion fires. The estimated apparent order of coal oxidation reaction was between 0.52 and 0.72, and increased with the initial temperature. The CO/CO₂ ratios became independent of the inlet O₂ concentration as the initial temperature increased. As the inlet O₂ concentration increased to 21%, the CO/CO₂ ratios for the three coals converged to the same value of 0.2. The experimental results in this study could be used for early detection and evaluation of a spontaneous heating and for better simulation of spontaneous heating in underground coal mines.

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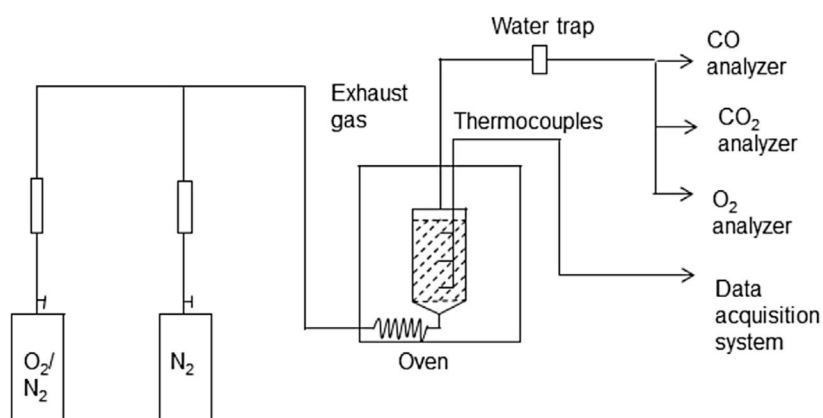


Fig. 1.
Schematic of experimental setup and measurement.

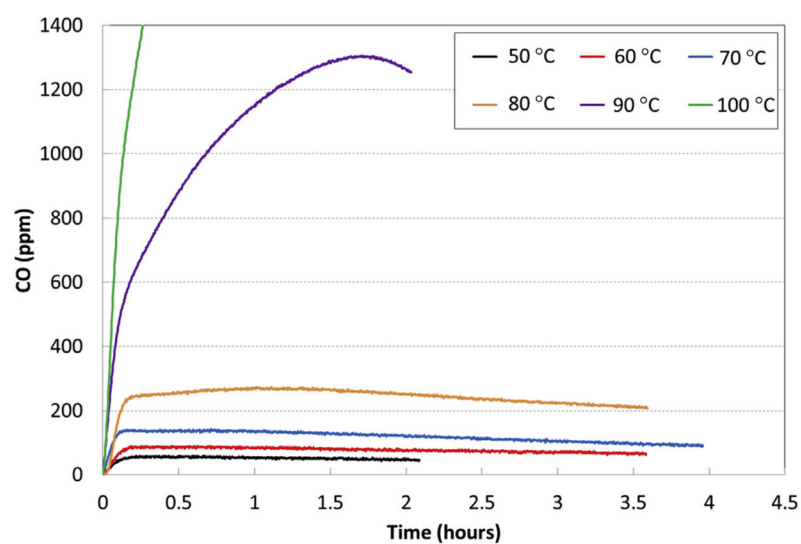


Fig. 2.
CO concentration for coal sample A at different initial temperatures, 21% O₂.

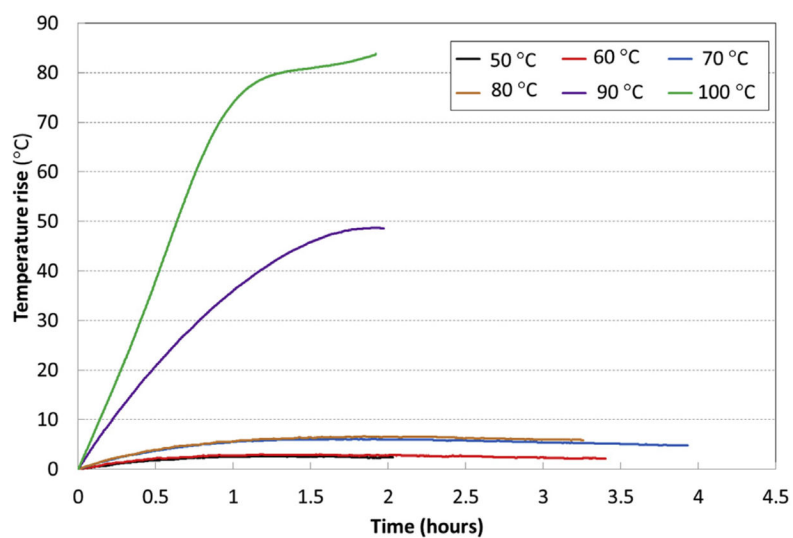


Fig. 3.
Center coal temperature rise for coal sample A at different initial temperatures, 21% O₂.

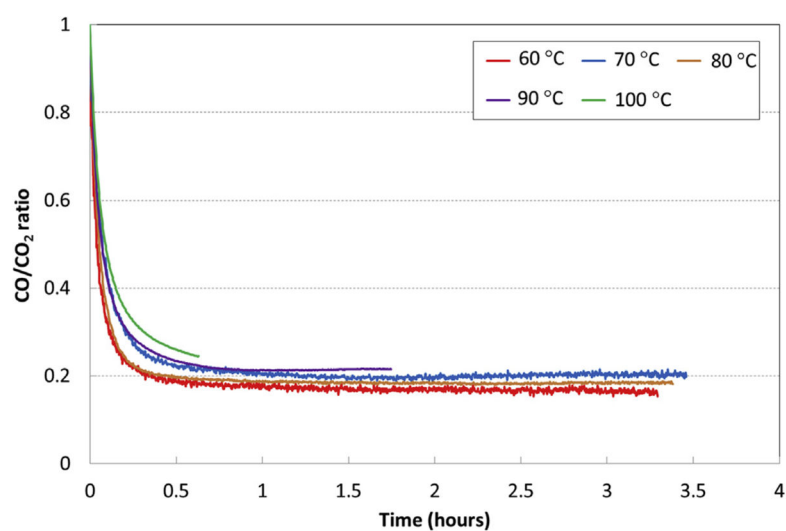


Fig. 4.
CO/CO₂ ratio for coal sample A at different initial temperatures, 21% O₂.

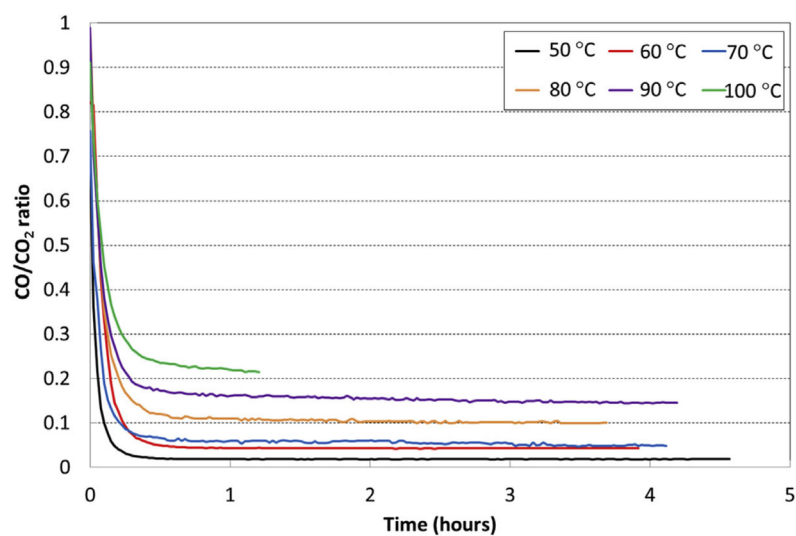


Fig. 5.
CO/CO₂ ratio for coal sample C at different initial temperatures, 21% O₂.

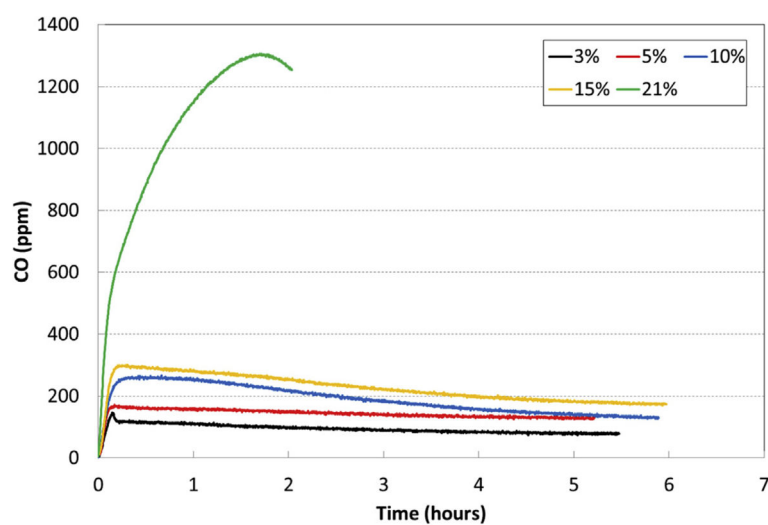


Fig. 6.
CO concentration for coal sample A at different O₂ concentrations, 90 °C.

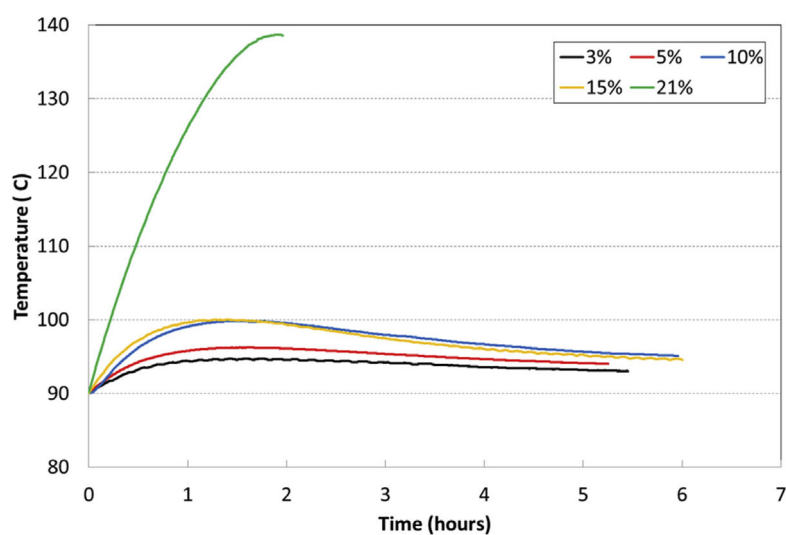


Fig. 7.
Temperature rise for coal sample A at different O₂ concentrations, 90 °C.

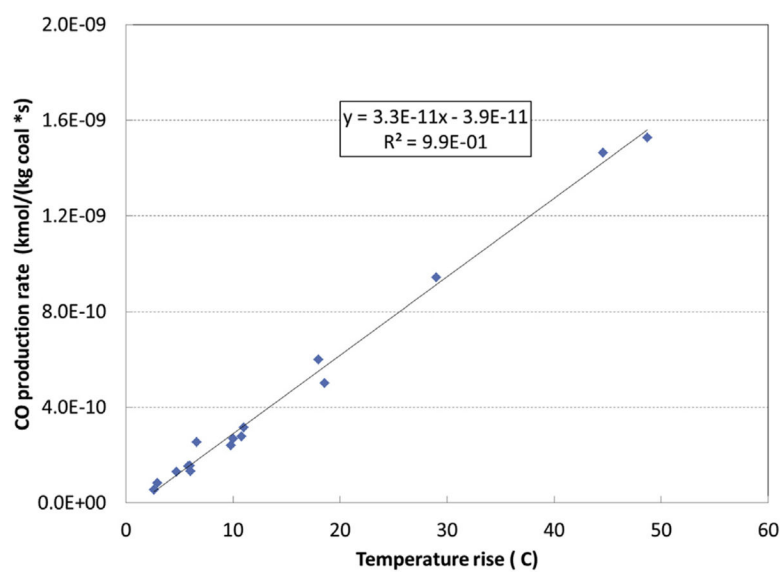


Fig. 8.
Maximum CO production rate versus maximum temperature rise for coal sample A.

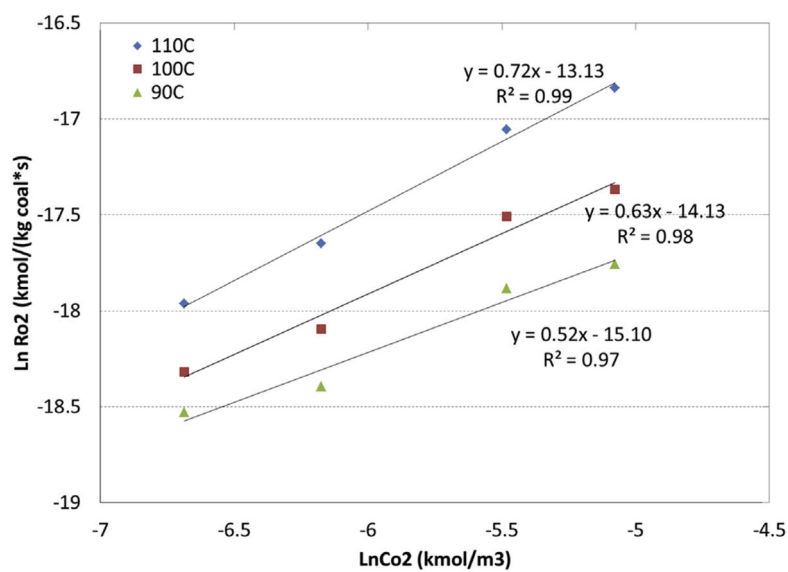


Fig. 9.
Reaction order for O_2 consumption for coal sample A.

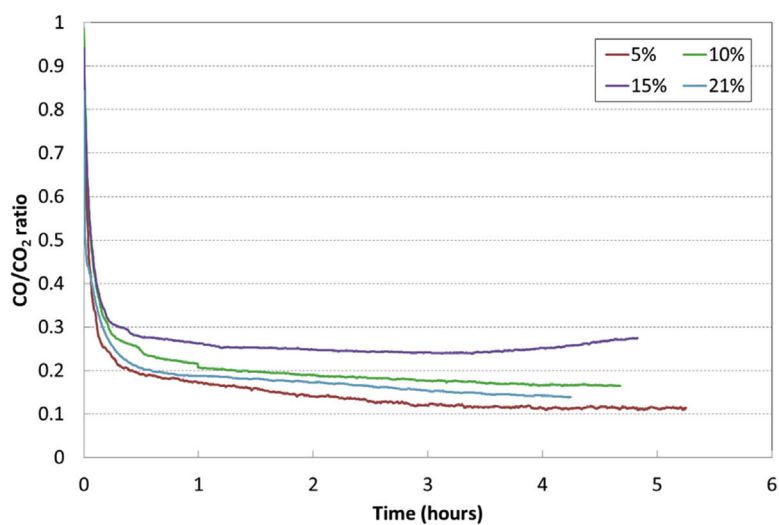


Fig. 10.
CO/CO₂ ratio for coal sample B at different O₂ concentrations, 90 °C.

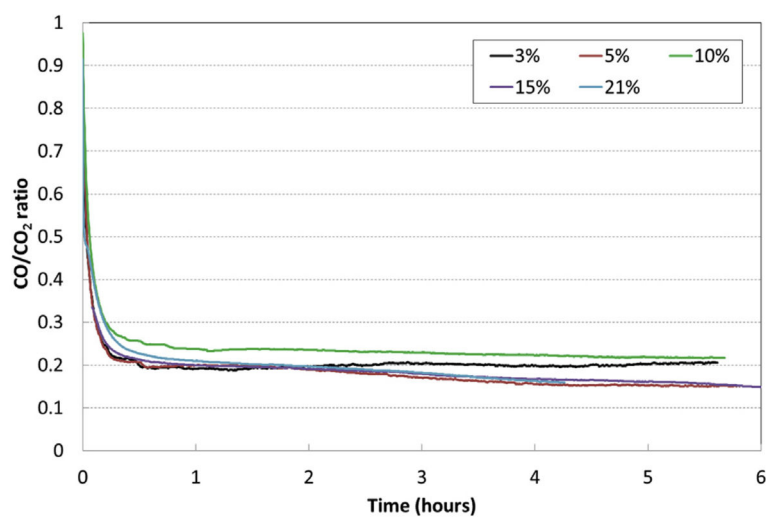


Fig. 11.
CO/CO₂ ratio for coal sample B at different O₂ concentrations, 100 °C.

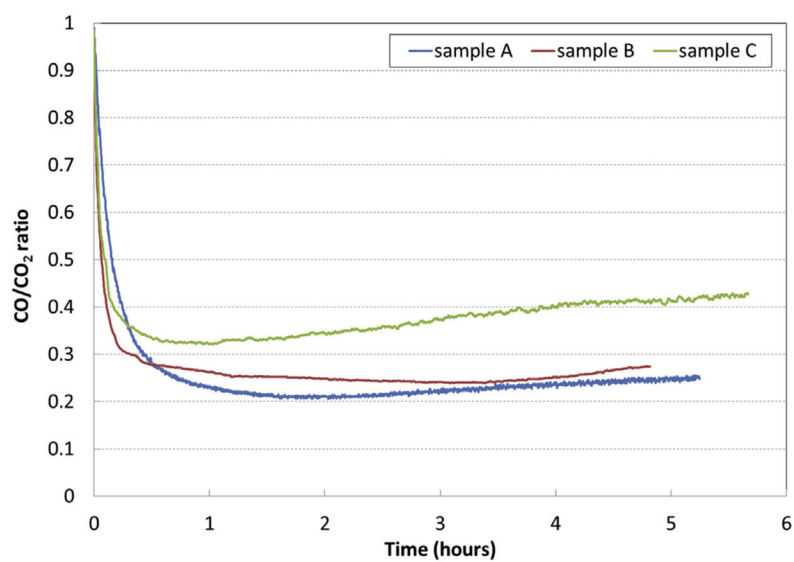


Fig. 12.
CO/CO₂ ratio for three coals, 90 °C, 15% O₂.

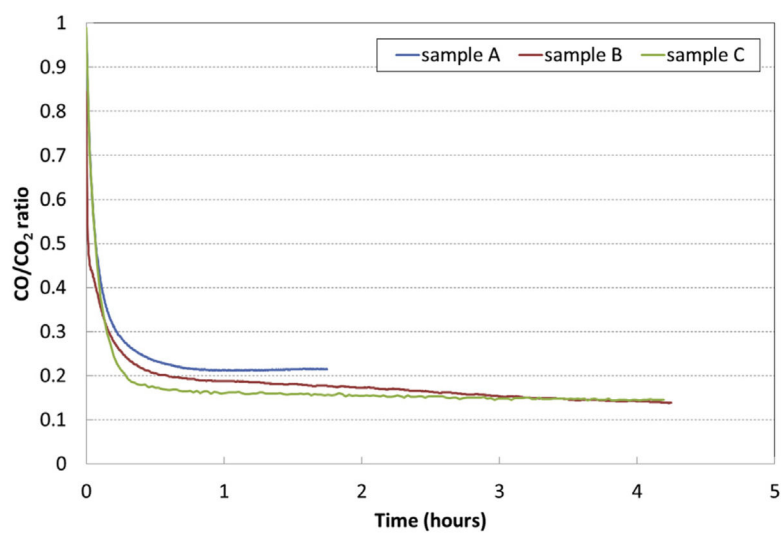


Fig. 13.
CO/CO₂ ratio for three coals, 90 °C, 21% O₂.

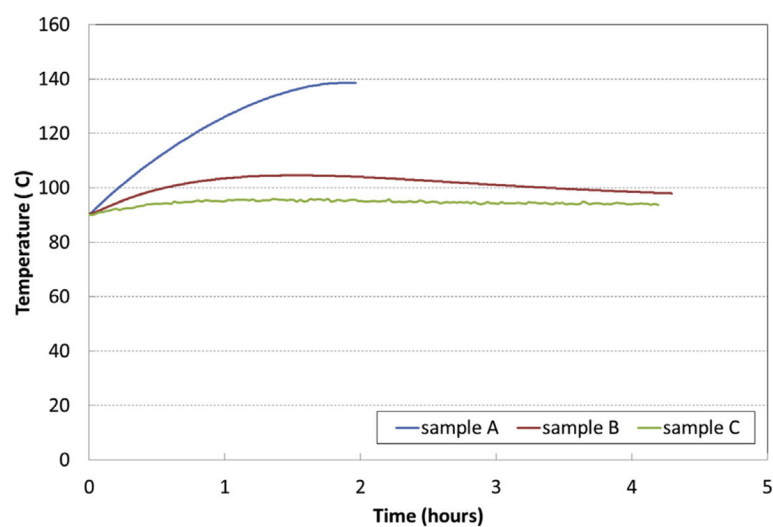


Fig. 14.
Center coal temperature for three coals, 90 °C, 21% O₂.

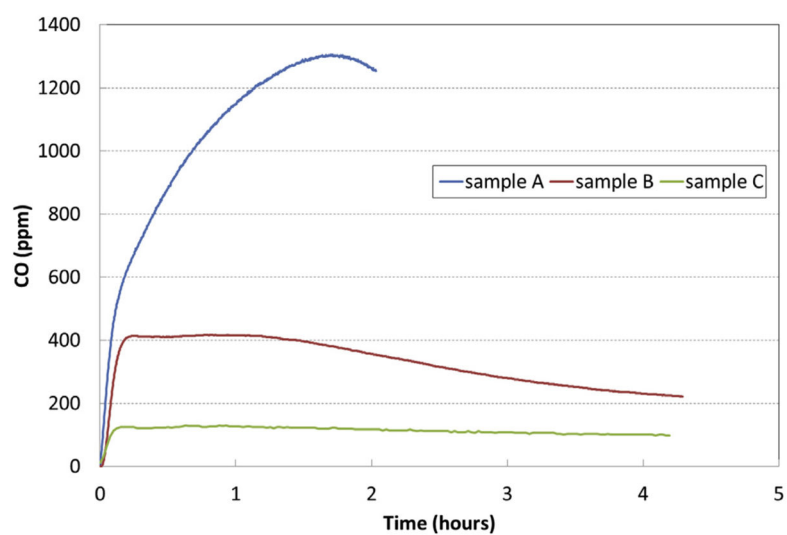


Fig. 15.
CO concentration for three coals, 90 °C, 21% O₂.

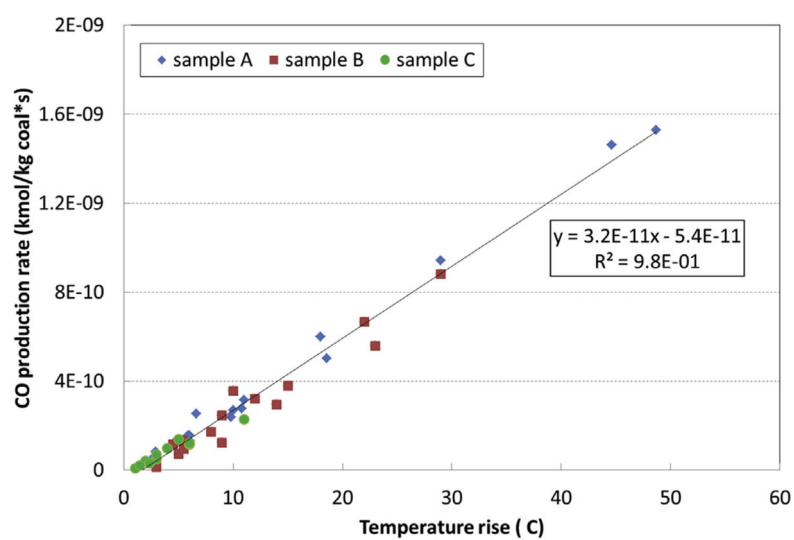


Fig. 16.
Maximum CO production rate versus maximum temperature rise for three coals.

Table 1Proximate and ultimate analyses of the coal samples.^a

Coal sample	A	B	C
Volatile matter (%)	44.03	40.83	38.40
Fixed carbon (%)	47.44	51.18	54.46
Ash (%)	8.53	7.89	7.14
Hydrogen (%)	5.47	5.61	5.83
Carbon (%)	77.79	79.64	82.72
Nitrogen (%)	1.48	2.02	1.57
Sulfur (%)	2.61	0.53	0.49
Oxygen (%)	12.65	12.20	9.39

^aProximate analysis is on dry basis, and the ultimate analysis is on dry ash-free basis.

Table 2

Activation energy and SHT of coal samples.

Coal sample	Activation energy (kcal/mol)	Calculated	Relative self-heating tendency
A	9.5	57	High
B	18.6	60	High
C	20.2	78	Medium